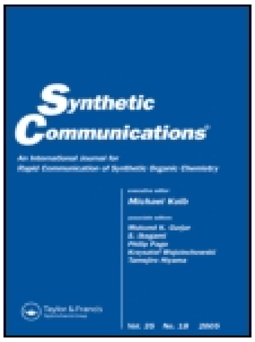

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FACILE SYNTHESIS OF 1, 3-DIARYL-PROPANONES THROUGH HECK REACTION

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Abstract: 1,3-diaryl propanones (1a-6a) and 1,3-diaryl-2-carbomethoxy-propanones (1b-6b) have been synthesized through facile palladium catalysed arylation of Baylis- Hillman adducts.

The palladium catalyzed vinylation of aryl halides (Heck reaction)[1] provides a convenient method for arylation at unsubstituted vinylic positions. For this reaction a multi-step mechanism involving cis-addition of ArPdX followed by syn-elimination of HPdX is well established. Though this reaction was first reported in early seventies, its synthetic value has been exploited extensively only during the last decade. Recently numerous modifications have been introduced to extend the synthetic applicability of this reaction such as solid phase synthesis,[2] reaction in aqueous medium,[3] effect of high pressure,[4] influence of quaternary ammonium salts,[5] as well as tertiary amines[6].

The Baylis-Hillman reaction[7] which involves the coupling of activated vinylic moiety with aldehydes in the presence of 1,4-diazabicyclo[2.2.2]octane (DABCO) is

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extensively used for the synthesis of α-hydroxy-alkyl or aryl-vinyl systems. The intermolecular Baylis-Hillman reactions are typically slow unless particularly reactive compounds or conditions are chosen. Recently we had reported microwave irradiated rate enhancement of this reaction[8]. In continuation of our studies on the synthetic utility of this reaction, we report herein palladium catalyzed arylation of Baylis-Hillman adducts. The Baylis-Hillman adducts 1-6 were subjected to Heck reaction in the presence of $Pd(OAc)_2$, PPh_3, and Et_3N to yield products 1a-6a and 1b-6b respectively (**Scheme 1**).

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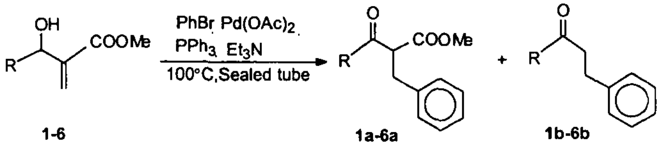
Scheme 1



The β-keto esters 1a-6a are formed by arylation of α-hydroxy-alkyl-acrylates with elimination of palladium hydride towards the hydroxy side, the enols thus formed undergo tautomerisation to the keto form. Further decarbomethoxylation of compounds 1a-6a afforded diaryl-propanones 1b-6b respectively, the yield of which increases with prolonged reaction time (Entry 7 & 8).

Thus the present report constitutes a simple method for the synthesis of 1,3-diaryl-propanones through Heck reaction which find wide synthetic applications. In view of natural occurrence of molecules having C_6-C_3-C_6 systems [9,10] and the ease of formation of α,β-disubstituted-β-keto esters the present study assumes greater importance.

Table:1 Heck reaction of Baylis-Hillman Adducts.

Entry	Compound No :	R-	Time (hrs.)	Product (%Yield)	
1	1	C_6H_5	7	1a (62)	1b (18)
2	2	4-(OMe)C_6H_4	7	2a (60)	2b (12)
3	3	2,5- $(OMe)_2C_6H_3$	7	3a (64)	3b (13)
4	4	3,4-$(OMe)_2C_6H_3$	7	4a (56)	4b (11)
5	5	CH_3CH_2	7	5a (58)	5b (16)
6	6	CH_3	7	6a (66)	6b (20)
7	1	C_6H_5	20	1a (48)	1b (28)
8	3	2,5-$(OMe)_2C_6H_3$	20	3a (51)	3b (30)

Experimental

General Procedure for Heck reaction of Baylis Hillman Adducts.

A typical reaction procedure involves heating a mixture of Baylis-Hillman adduct (2mmol), $Pd(OAc)_2$ (0.02mmol), PPh_3 (0.04mmol) and Et_3N (2.5mmol) in a sealed tube for the period mentioned in Table 1. The reaction mixture was extracted with ethyl acetate,washed with dilute HCl (10%, 5ml), water, brine and finally dried over anhydrous Na_2SO_4. The products were separated by column chromatography over silica gel (100-200 mesh) using petroleum ether/ethyl acetate as eluant and were characterized through spectral studies.

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Compound 1a :IR (ν_{max} neat) :3062,3030,2955,1743,1687,1600,1448,1236, 1170,1030 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) : δ 7.17-7.96 (10H, m), 4.6 (1H, t), 3.64 (3H, s), 3.36 (1H, dd J=7.6 & 14), 3.32 (1H, dd, J=7.6 & 14)

Compound 1b :IR (ν_{max} $CHCl_3$) : 3060,3024,1684,1607,1452,1221 cm^{-1}

^{1}H NMR (500 MHz, $CDCl_3$) :δ 7.2-7.9 (10H, m), 3.2 (2H, t J=7.5Hz), 3.1(2H,t J=7.5Hz).

Compound 2a :IR (ν_{max} neat) 3060, 3025,2948,1740,1682,1610,1228 cm^{-1}

^{1}H NMR (500 MHz, $CDCl_3$) :δ 7.2-7.6 (9H, m), 4.68 (1H, t J=7.5Hz), 3.97 (3H, s), 3.65 (3H, s) 3.35 (1H, dd J=7.5 & 14.2 Hz), 3.25 (1H, dd J=7.5 & 14.2 Hz)

Compound 2b :IR (ν_{max} neat) 3065,3032,1682,1596,1456,1218 cm^{-1}

^{1}H NMR (500 MHz, $CDCl_3$) :δ 7.1-7.5 (9H, m),3.96 (3H, s), 3.2 (2H, t J=7.5Hz), 3.08 (2H, t J=7.5Hz)

Compound 3a :IR (ν_{max} neat) : 3005,2949,2837,1739,1680,1501,1224 cm^{-1}

^{1}H NMR (500 MHz, $CDCl_3$) :δ 6.82-7.56 (8H, m), 4.70 (1H, t J=7.25Hz), 3.81 (3H, s), 3.77 (3H, s), 3.64 (3H, s) , 3.32 (1H, dd J=7.25 & 13.9 Hz), 3.22 (1H, dd J=7.25 & 13.9 Hz)

Compound 3b :IR (ν_{max} neat) : 2920,2850,1682,1597,1280,1163,1025 cm^{-1}

^{1}H NMR (500 MHz,$CDCl_3$): δ 6.8-7.5 (8H, m), 3.84 (3H, s), 3.79 (3H, s), 3.32 (2H,t J=7.6Hz), 3.02 (2H, t J=7.6Hz).

Compound 4a :IR (ν_{max} neat) : 3058,2960,2841,1740,1680,1600,1518 cm^{-1}

^{1}H NMR (500 MHz, $CDCl_3$) : δ 6.2-7.6 (8H, m), 4.61 (1H, t J=7.5Hz), 3.92 (3H, s), 3.9 (3H, s), 3.6 (3H, s), 3.35 (1H, dd J=7.5 & 14.2 Hz), 3.30 (1H, dd J=7.5 & 14.2Hz)

Compound 4b :IR (ν_{max} neat) : 2925,2846,1678,1602,1520,1280,1025 cm^{-1}

^{1}H NMR (500 MHz, $CDCl_3$) :δ 6.9-7.5 (8H, m), 3.94 (3H, s), 3.92 (3H, s), 3.26 (2H, t J=7.5Hz), 3.06 (2H, t J=7.5Hz).

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Compound 5a :IR (ν_{max} neat) 3032,2920,2848,1749,1716,1604,1499,1170 cm^{-1} ^{1}H NMR (500 MHz, CDCl$_3$) :δ 7.1-7.28 (5H, m), 3.8 (1H, t J=7.5Hz), 3.68 (3H, s), 3.3 (1H,dd J=7.5 & 13.9Hz), 3.25 (1H,dd J=7.5 & 13.9Hz), 2.34 (2H, q J=7.2Hz), 0.98 (3H, t J=7.2Hz).

Compound 5b :IR (ν_{max} neat) : 3032,2933,1716,1520,1459,1227,1117 cm^{-1} ^{1}H NMR (500 MHz, CDCl$_3$) :δ 7.1-7.28 (5H, m), 2.9 (2H, t J=7.5Hz), 2.75 (2H, t J=7.5Hz), 2.42 (2H, q J=7.2Hz), 1.06 (3H, t J=7.2Hz).

Compound 6a :IR (ν_{max} neat) :3020,2950,1742,1720,1610,1490,1238 cm^{-1} ^{1}H NMR (60 MHz, CDCl$_3$) :δ 7.2 (5H, m), 3.82 (1H, t J=7.5Hz), 3.7 (3H, s), 3.2 (2H, d J=7.5Hz), 2.2 (3H, s).

Compound **6b** :IR (ν_{max} neat) : 3024,2955,1725,1600,1498,1451,1246 cm^{-1} ^{1}H NMR (60 MHz, CDCl$_3$) :δ 7.2 (5H, m), 2.94 (2H, t J=7.4Hz), 2.8 (2H,t J=7.4Hz), 2.3 (3H, s).

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